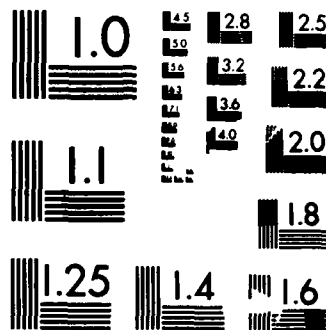


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The transient molecule HBO has been studied by ab initio theoretical electronic structure techniques. The heat of formation of this molecule is predicted to be about -60 kcal/mole, more than 10 kcal/mole lower than previous estimates. This number is arrived at independently by fourth order perturbation theory calculations and by multireference configuration interaction (MRCI) calculations both with a double-zeta plus polarization basis set. The activation barrier for the H + HBO hydrogen atom abstraction reactions is found to be about 20 kcal/mole and this reaction is predicted to be endothermic by about 8 kcal/mole.

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**BY**

**MICHAEL PAGE**

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## REACTIONS OF HBO: A THEORETICAL STUDY

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Detailed knowledge of the homogeneous gas phase combustion chemistry of boron is a necessary, if not sufficient, prerequisite to developing predictive capabilities for the use of boron as a fuel in air breathing propulsion systems. Unfortunately, the base of knowledge of boron/hydrogen/oxygen chemistry is quite limited compared to that for hydrocarbon/oxygen systems. Not only are the detailed rate coefficients unavailable, but little is known about the basic thermochemistry of the intermediate species. Indeed not much is known about even the identity of the intermediate species. The situation, including the need for more knowledge of basic homogeneous chemistry, was summarized a few years ago by Faeth<sup>1</sup>.

More recently, a joint effort between Aerodyne Research, Inc. and Princeton University<sup>2</sup> has given birth to a tentative model of the homogeneous combustion process. The immediate goal of the Aerodyne/Princeton model is the identification, through sensitivity analysis, of hypothetical key molecules, radicals and reaction rates for further detailed study. Improved rate parameters can then be fed back into the model. This is of course an iterative process which may or may not be rapidly convergent. Nevertheless, key reactions have been identified. Prominent among these are reactions which produce BO from HBO:



The transient molecule HBO appears to be an important species. It has only recently been experimentally identified<sup>3</sup>. No experimental effort has yet been successful in its synthesis and detection to the degree that its reactions can be monitored.

We describe here theoretical calculations directly pertinent to reactions 1 and 2 above and indirectly pertinent to all of the above reactions. The quantitative results are tentative, but it appears that some conclusions can be drawn:

- A. the endothermicity of reaction 1 (i.e. the strength of the BH bond in HBO) is at least 10 kcal/mole greater than previous estimates.
- B. rephrasing A, the heat of formation of HBO is at least 10 kcal/mole lower than previous estimates.
- C. reaction 2 is endothermic, not exothermic.
- D. the activation barrier for reaction 2 is fairly substantial (i.e. greater than 15 kcal/mole)

E. as a consequence of conclusion B, The enthalpies of reaction for 3 and 4 are notably different from previous estimates.

The calculations leading to these conclusions are now discussed in more detail. We begin with a discussion of the heat of formation of HBO, and follow this with a discussion of the computation of reaction energetics for reaction 2 including the transition state complex. Finally, we discuss future plans for the completely ab-initio determination of the temperature dependent rate constants for the above reactions.

The heat of formation of HBO ( $\Delta H_f^{298}$ ) is listed in the JANAF tables as  $-20. \pm 20$  kcal/mole<sup>4</sup>. The value used in reference 2 is  $-47.2. \pm 3$ . We have calculated this quantity using two different theoretical approaches. In the first approach, we optimized the geometrical structures and computed the zero point vibrational energies of HBO and BO at the Hartree-Fock level of theory using a double-zeta plus polarization<sup>5</sup> (DZP) basis set. Subsequently, electronic energies were calculated using fourth order perturbation theory including all single, double triple and quadruple excitations. From these results, we compute a BH bond energy in HBO of 110.3 kcal/mole. It should be noted however that quantum chemistry calculations of this sort consistently underestimate bond strengths, but do so in a way which can be characterized by bond type and is fairly insensitive to the secondary chemical environment<sup>6</sup>. This suggests the use of a bond correction factor. We have calculated such a bond correction for BH bonds in boron hydrides<sup>7</sup> and find that this bond strength is underestimated by about 2.5 - 3.0 kcal/mole at this level of theory. Applying this correction factor gives a BH bond strength in HBO of about -113 kcal/mole and (assuming  $\Delta H_f^{298}$  (BO)=0.0 kcal/mole) a heat of formation of about -61 kcal/mole. In a separate calculation using multireference configuration interaction techniques and a DZP basis set, the enthalpy of reaction 2 was calculated to be 8. kcal/mole. Assuming again a value of zero for the heat of formation of BO, we obtain a value for  $\Delta H_f^{298}$  of HBO, -60 kcal/mole, in good agreement with the perturbation theory value of -61 kcal/mole.

The electronic structure methods leading to these two estimates for the heat of formation of HBO are quite different in their approach to the treatment of electron correlation. It is true that both of these calculations use the same finite basis set, however they use distinct approaches to reducing the liability of an incomplete basis set. For the perturbation theory calculations, a bond correction factor, determined from BH bonds in boron hydrides was used. For the configuration interaction calculations, only isogyric energy comparisons were made. That is, comparisons were made only between species with the same number of electron pair bonds. One is essentially then calculating a differential bond energy as opposed to an absolute bond energy, with consequently smaller error.

Perturbation theory based electronic structure techniques such as those mentioned above are only appropriate for treating molecules which are in the vicinity of their equilibrium structures. This is because the zero order level of the perturbation expansion is not capable of properly describing chemical bonds being formed and broken. For these reactions, we use techniques based on a multiconfiguration (MCSCF) formalism. In particular, active electrons and active molecular orbitals are chosen which are expected to undergo substantial changes during the course of the reaction. Electron correlation is then included in this subspace in a consistent and well defined manner. During the course of reaction 2 above, the BH bond is

being broken, the HH bond is being formed, and the radical site is moving from the hydrogen atom to the BO moiety. This suggests a three electron/three active orbital treatment. The three orbitals at the reactant are the BH bonding and antibonding orbitals and the hydrogen atomic orbital. At the product side, the three orbitals are the HH bonding and antibonding orbitals and the BO radical orbital. The orbitals smoothly transform from the reactant set to the product set during the course of the reaction. There are eight configurations in the resulting MCSCF expansion.

Using analytical gradient techniques, the structures of the reactant, transition state and product for reaction 2 have been fully optimized. The MCSCF/DZP structural parameters are shown in Table I. The reaction is a collinear abstraction thus only bond lengths are shown. Note that at the transition state, the HH bond is stretched by about 20% and the BH bond is stretched by about 28%. This is consistent with the observation that the reaction is endothermic, but not very endothermic. Final energetics are obtained by using the MCSCF orbitals described above as reference orbitals in a large scale configuration interaction treatment. A configuration expansion is generated by including each of the eight reference MCSCF configurations and in addition including all configurations which result from either a single or double electron replacement from an occupied orbital into one or two of the unoccupied orbitals. This procedure generates 106,422 doublet configurations in the CI expansion. At this multireference CI/DZP level, the barrier to the reaction is found to be 20 kcal/mole and the endothermicity, 8 kcal/mole.

The calculated activation barrier of 20 kcal/mole for reaction 2 may be lowered somewhat upon treatment with a more flexible basis set, but it is not expected to be lowered by more than, say, three or four kcal/mole. Barriers for the reactions  $H_2 + CN \rightarrow H + HCN^8$  and  $H_2 + C_2H \rightarrow H + C_2H_2^9$  calculated at a similar level of theory to that presented here were found to be within about 2 kcal/mole of experimental activation energies. These are analogous to the reverse of reaction 2.

We plan to improve the overall energetic predictions for reaction 2 by performing calculations with a triple-zeta plus polarization basis set. In addition, we plan to compute molecular vibrational properties along the reaction pathway and use these for a canonical variational transition state theory calculation of the temperature dependent rate constant. Calculations of the activation parameters for reaction 3 are also currently underway. It is expected that in the absence of experimental rate information, calculations such as these will prove invaluable to modelling attempts. If experimental information is available over a limited temperature range, then these predictions will serve to extrapolate rate constants to temperature regimes of interest in combustion.

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Table I  
MCSCF structural parameters  
for hydrogen atom abstraction from HBO

	$R_{HH}(\text{\AA})$	$R_{BH}(\text{\AA})$	$R_{BO}(\text{\AA})$
$H + HBO$	$\infty$	1.183	1.191
$H - -H - -BO$	0.905	1.519	1.191
$H_2 + BO$	0.756	$\infty$	1.192

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